

Removal of cadmium from aqueous solutions by eggshell as low-cost adsorbent

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ABSTRACT

Cadmium is one of the environmental toxic elements used in various industries such as electroplating, plasticization, battery making, electrically, communications, dyeing, fertilization and alloy making and its adverse health effects such as kidney and lung damage, types of cancer, hypertension Blood and anemia have been proven in humans. Therefore, its entry into the body through water, air and food causes disturbance to the body's natural activities, so it is of great ecological and biological importance. The aim of this research was to investigate the cadmium removal using eggshell and specifying the adsorption isotherms and kinetics. In this research, cadmium solutions were prepared from cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$). The pH amount of the solutions was adjusted by Sodium Hydroxide and Acetic Acid at a concentration of 0.1 mol/L. The pH of the solution was adjusted in the amount of 2 to 10. To describe the data, kinetics models of Ho et al. and Lagergren were used. Isotherm models of Langmuir and Freundlich were used to describe the laboratory data in the adsorption process. The results indicated that the most capacity of eggshell in cadmium adsorption happened at pH=8 and contact time 120 minutes. Investigation of adsorption isotherms showed that Freundlich isotherm with a correlation coefficient of 0.97 is more consistent with cadmium adsorption by eggshell. Comparing the correlation coefficient between measured data and obtained amount from Ho et al model and Lagergren model showed that the Ho et al model with a correlation coefficient of 0.96 describes experimental data better.

Keywords: Cadmium, Ho et al., Lagergren, Langmuir, Freundlich.

Introduction

The existence of reliable and safe water sources without toxic and dangerous pollutants is an initial and basic needs for a healthy and sustainable society. Among the sources of water pollutants are heavy metals that enter the ecosystem through the discharge of industrial effluents, fuel consumption, urban wastewater discharge, sewage sludge consumption and so on. Heavy metals are not capable of being separated to compounds with degree of less toxicity and accumulate in the environment, and are

extremely dangerous. The degree of toxicity of metals is different in the various conditions and is influenced by factors such as concentration, environmental conditions, contact time and other physical, chemical and biological factors ^[1]. Cadmium is one of these heavy metals. The solubility of this metal and its compounds is higher than that of other metals and tends to accumulate in living tissues. Cadmium consumption by humans can cause kidney damage and cardiovascular disease, osteoporosis, blood disease. In addition, cadmium is one of the metals absorbed by the plant through irrigation, thus increasing the likelihood of its direct use by humans ^[2]. There are several ways to remove cadmium from aqueous solutions. The adsorption method has attracted the attention of all researchers because of its low cost. There have been many studies on the removal of cadmium from aqueous solutions using various adsorbents, that here some of them are presented in the summary. Maleki and Shirzad Sinoni (2012) investigated the potential of acid modified zeolite for cadmium adsorption in aqueous environment ^[3]. In this study, in order to enhance the

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zeolites' sorption capacity for cadmium, these researchers treated natural clinoptilolite with sulfuric acid solutions and investigated the sorption of cadmium to acid-modified clinoptilolite by a series of batch experiments. The batch method has been employed using metal concentrations in solution ranged from 25 to 100 mg/l and adsorbent ranged from 0.2 to 1.8 g/l. The influence of acid concentration, contact time, solution pH, adsorbent particle size, initial cadmium concentration and adsorbent mass has been studied. It was found that the acid modified clinoptilolite exhibits higher adsorption to cadmium than unmodified clinoptilolite and adsorption of the cadmium is influenced by several parameters such as cadmium initial concentration, adsorbent dosage and solution pH. Maximum absorption efficiency was achieved at pH of 6. Meanwhile maximum absorption efficiency of acid modified clinoptilolite in cadmium removal shows improvement due to 1 molar sulfuric acid. The equilibrium adsorbed amount also increased with the initial concentration of the metal ions, as expected. Among the models tested, namely the Langmuir, Freundlich, and Dubinin Radushkevich isotherms, the biosorption equilibrium for cadmium was best described by the Langmuir and Freundlich models. Mean free energy of adsorption (15.8 kJ mol^{-1}) indicates that adsorption of cadmium by acid-modified clinoptilolite follow a chemisorption mechanism. Adsorption capacities of the acid- modified clinoptilolite for cadmium increased as the particle size decreased down to 0.5 mm in diameter, but no difference was observed for a diameter less than 1.5 mm. The best results in terms of efficiency are obtained for the clinoptilolite modification with 1 molar sulfuric acid and it was more favorable than natural clinoptilolite in removing cadmium and thus was a better adsorbent as low-cost alternatives in wastewater treatment for cadmium removal. Hamidpour et al (2018) investigated the biosorption of cadmium from aqueous solutions by shrimp shell [4]. In this study, the adsorption of Cd on shrimp shell was studied as a function of pH (Cd concentration: 8.0 mg L^{-1}) in the range of 3.0-8.0, and as a function of metal concentration (Cd concentration in the range of 15-100.0 mg. L^{-1}) using a 24h batch equilibration experiments. The amounts of Cd sorbed on the adsorbent were calculated from the difference between the metal concentration in the blank and equilibrium concentration of Cd in the solutions. Chemical species of Cd(II) in the solutions was also predicted using Visual MINTEQ, a computer code developed to simulate equilibrium processes in aqueous systems. Infrared spectrums of untreated and Cd-loaded adsorbent were obtained using a Fourier transform infrared spectrometer. The results of pH dependent experiments showed that the percent removal of Cd on the sorbent increased with the increase of suspension pH. The experimental data showed that shrimp shell used in this study removed more than 95% Cd from solution at pH=7.5. The Freundlich and Langmuir isotherms were described satisfactorily equilibrium data. Maximum sorption capacity (q_{max}) of the sorbent was 5.1 mg. g^{-1} . Pseudo second order kinetic model provided a perfect fit for the kinetic data of Cd sorption onto

shrimp shell. Biosorption kinetics of Cd consisted of two steps: An initial rapid step where adsorption was very fast. The second phase is the gradual biosorption stage before the Cd uptake reached equilibrium. The equilibrium was achieved in 30 min for initial metal concentration of 5 mg. L^{-1} and in 240 min for initial metal concentration of 50 mg. L^{-1} where 91 % and 92 % of Cd were adsorbed, respectively. Based on the estimates obtained by Visual MINTEQ, the Cd^{2+} and Cd(OH)^+ species were the dominant species present in solutions in $\text{pH} \leq 8.5$ and $\text{pH} \geq 8.5$, respectively. Infrared spectrum analysis of adsorbent before and after adsorption showed that the N atoms of the amine functional groups played a major role in shrimp shell for adsorption of Cd. Based on the equilibrium sorption and kinetic information obtained for Cd removal by this sorbent, it may be concluded that shrimp shell is an effective sorbent for Cd and may be considered for environmental remediation in future studies. Ahmady Asbchin (2013) investigated the biosorption of Cd (II) from aqueous solution by *Fucus Serratus* [5]. In this research it became clear that a key role in the uptake of cadmium ions alginate surface active groups, especially carboxyl foundations are responsible. Firstly, the characterization of the surface functional groups was performed with the method, a qualitatively analysis with the study of FT-IR spectrum. The equilibrium time was about 300 min and the adsorption equilibrium data were well described by the Langmuir's equation. The maximum capacity has been extrapolated to $0.85 \text{ mmol. g}^{-1}$. Finally; the efficiency of this biosorbent in natural tap water for the removal of cadmium was also investigated. Shahidi et al. (2015) evaluated the natural adsorbent *Luffa cylindrical* for the removal of cadmium (II) from aqueous environments. In this study, the effects of pH, contact time, adsorbent dosage, and initial solution concentration on the uptake of metal ions by the adsorbent in the batch operation were examined [6]. Langmuir and Freundlich isotherm models were used to investigate the adsorption equilibrium. The adsorption behavior of Cd(II) ions fitted both isotherms but followed the Langmuir isotherm most precisely ($R^2=0.987$), with a maximum adsorption capacity of 6.711 mg/g . Cadmium removal in the continuous flow mode using a fixed bed column was also studied. The effect of operating parameters such as flow rate and inlet Cd(II) concentration on the sorption characteristics of *Luffa* were determined by assessing the breakthrough curve. The data confirmed that the total amount of sorbet Cd(II) and equilibrium Cd(II) uptakes decreased with increasing flow rate but increased with increasing inlet Cd(II) concentration. The Adams–Bohart model was applied to the experimental data to predict the breakthrough curves and to determine the characteristic parameters of the column useful for process design. Results showed that the natural *Luffa* adsorbent was capable of efficiently removing cadmium from water. Motamedi et al (2014) investigated the kinetics and isotherms of adsorption of Cd(II) ions on nanoclay from aqueous solution [7]. This study was implemented under laboratory conditions in single batch system by adsorption under various environmental conditions such as pH, contact time, adsorbent

dose and cadmium concentration. The kinetics of Cadmium adsorption was determined based on Ho et al & Lagergren. Then Langmuir and Freundlich coefficient were determined based on optimum conditions. The Result of this study was showed with increasing of pH from 2 to 8; the adsorption efficiency will be increased. With increasing contact time adsorption efficiency increased. It was also fund with increasing amount of nanoclay adsorbent, efficiency increased. The results revealed that the results of this research for nanoclay adsorbent is closed to fit Ho et al and Lagergren kinetic and Freundlich isotherm Based on data obtained in this study it can be concluded that adsorption by nanoclay is an efficient and reliable method for cadmium removal from liquid solutions. Farzi et al (2018) investigated the removal of Cd from aqueous solution using sugarcane straw nanostructure^[8]. In this study, the effects of operation conditions including pH, contact time, adsorbent loading, and initial ion concentrations were examined . The absorption-desorption process was also carried out in five cycles. The results showed that optimum pH for cadmium adsorption is 5, the removal percentage became 94.5 %. The equilibrium time after 10 minutes obtained. With an increase in adsorbent dosage from 0.1 to 0.5 g, the removal percentage from became 88.8% to 94.5% increased. the increase of adsorbent dosage from 0.5 to 2 g did not have a significant effect on removal percentage. With increase in Cd concentrations (5, 10, 15 and 20 mg/L), removal percentage decreased from 96% to 90%. Comparing the adsorption isotherms showed that the Langmuir model, with R² value of 0.995 had a better fitting and description of adsorption data than other models. The results of the desorption experiments showed that sugarcane straw adsorbent could reused up to 5 cycles. The result of this study showed that sugarcane straw nanostructure is an effective adsorbent for cadmium removal from aqueous solution. Shamohammadi et al (2008) investigated the removal of cadmium from water using improved rice husk^[9]. This paper studies the effect of different molarities of sodium bicarbonate on enhanced absorption capacity of rice husk to remove cadmium in low concentrations. Maximum absorption efficiency was achieved at a pH of 6 and absorption equilibrium time was 1.5 hours. Results of chemical experiments and photography by electronic microscope from improved rice husk revealed a good relationship to exist between number and average diameter of absorber pores, on the one hand, and absorption efficiency, on the other. Meanwhile maximum absorption efficiency of rice husk in cadmium removal was 99.1 percent which shows improvement due to 0.3 molar sodium bicarbonate. In this study, kinetic absorption models were also studied. Both Lagergren (1898) and Ho et al. (1996) models satisfactorily described data with a confidence level of 95 percent; however, the latter model was found superior in this respect^[10]. Comparison of the coefficients calculated here with those reported in other models showed a faster cadmium absorption rate by improved rice husk due to 0.3 molar sodium bicarbonate. Divband et al (2013) investigated the efficiency of cedar (*zizyphus spinachristi*) leaf and its fly ash in removing cadmium (II) from water by batch

adsorption^[11]. In this study, two new absorbents (*zizyphus spinachristi* leaf and its fly ash) were studied for adsorption of cadmium from aqueous solutions using batch experiments. The effect of contact time, pH, and amount of adsorbent on adsorption efficiency was evaluated and the best kinetic and isotherm model was determined. Results showed that optimal absorption of pH was 5 and 6 for *zizyphus spinachristi* leaf and its fly ash, respectively. The equilibrium time was 45 min for *zizyphus spinachristi* leaf and 30 min for ash. Adsorption efficiency was increased by increasing the adsorbent dose. By comparing the parameters of isotherm models, it was observed that the cadmium adsorption capacity of fly ash (4.27 mg/gr) was higher than that of *zizyphus spinachristi* (3.91 mg/gr). Amini et al (2019) investigated the potential of cadmium ions removal from aqueous solutions using date-palm leaf ash^[12]. In this study, the studied variables were pH (2-7), Cd (II) ion concentrations (50 – 350 mg/l) and adsorbent dose (0.1 – 14 g/l) in batch systems. The optimum pH for the removal of Cd (II) ions was equal to 4. Investigation of the effect of adsorbent dose showed that the removal efficiency increased with the increase of adsorbent dose from 0.1 to 11 g/l, and after that the removal efficiency was stabled with the increase of adsorbent dose. The highest removal efficiency was obtained at 60 minutes in 100 mg/l Cd(II) concentration. According to results, optimum removal efficiency of Cd(II) in pH 4, adsorbent dose of 11 g/l and Cd(II) ions concentration of 100 mg/l was obtained as 92.36%. It was concluded that the date-palm leaf ash had a good potential as an adsorbent for the removal of toxic heavy metals, such as cadmium, from aqueous solutions. The objective of this study was to investigate the cadmium removal using eggshell and determining the adsorption isotherms and kinetics.

Materials and Methods

eggshells were obtained from kitchen of the Aburaihan college, university of Tehran. The eggshells were washed twice times with water and twice with distilled water and dried in an oven at 30°C for 24 hours. The eggshells were powdered by mechanical grinding machine and used in the laboratory for cadmium removal. Storage solutions (1000 mg/L) were prepared by using cadmium nitrate (Cd(NO₃)₂·4H₂O). Then solutions were made at concentrations of 3, 7, 12, 19, 30, 45 and 60 mg/L of the main storage solution. In all experiments, the volume of the solution used will be 60 ml. The pH values of the solutions were adjusted by Sodium Hydroxide and Acetic Acid at a concentration of 0.1 mol/L. The pH of the solution was adjusted in the amount of 2 to 10. In order to determine the optimum pH of cadmium adsorption by eggshell, first 10 beaker of 500 ml washed with distilled water and in each beakers is poured 2 gram of eggshell powder. Then add 200 ml of solution with a cadmium concentration of 12 mg/L to each beaker. The solution is placed at 30°C temperature for 80 minutes on an incubator shaker at a speed of 200 rpm. Then, the eggshell powder separation from the solution was done by the filter paper and the concentration

of the solution is determined by using Atomic Absorption Spectrophotometry Perkin Elmer 4100. To determine of adsorbent optimal mass, the amount of 1, 2, 4, 6, 9, 12, 19, 30, 40, 52 and 60 g of eggshell powder is added to 100 mL of solution at a concentration of 30 mg/L. The pH of the solution is adjusted to the optimum amount and then placed on a shaker at 200 rpm for 80 minutes. Then, the adsorbent separation from the solution was done by the filter paper and the cadmium concentration of the solution is specified. Obtaining adsorption isotherm is a suitable method for determining adsorbent potentials. The adsorption isotherm curves are able to quantitatively evaluate the behavior and adsorption performance of natural adsorbents for a substance at a time [13]. Equilibrium adsorption isotherms are equations that show the distribution of matter adsorbed between the soluble and adsorbed phase in the equilibrium condition and is a characteristic for the system at a specific temperature. To describe the equilibrium state, two parameters q_e and C_e are used, where q_e is the amount of matter adsorbed per unit weight of the adsorbent and C_e is the concentration of the remaining part in the solution [14]. To perform adsorption isotherm tests, add 2 gram of eggshell powder to 200 ml of solution at various concentrations (3, 7, 12, 19, 30, 45 and 60 mg/L), and the shaker is placed at a speed of 200 rpm for 80 minutes. Then, the adsorbent separation from the solution was done by the filter paper. Then the Langmuir and Freundlich models are used to describe the data. The Langmuir model shows a monolayer adsorption on the homogeneous surface without the reaction between adsorbed molecules and uniform energies of adsorption on the surface [13]. The Langmuir adsorption isotherm is represented by Equation 1 [14].

$$q_e = \frac{q_e b c_e}{k_l + k_l c_e} \quad (1)$$

Concentration of adsorbed substance in equilibrium condition in the liquid phase (mg/L) = C_e ; The amount of ion adsorbed per unit mass of the adsorbent in equilibrium condition (mg/g) = q_e ; Adsorption capacity in solid phase (mg/g) = b ; Adsorption coefficient = k_l Freundlich isotherm is an experimental model for explaining the multilayer adsorption by heterogeneous energy distribution with the reaction between the adsorbed molecules. The Freundlich adsorption isotherm is represented by Equation 2 [15].

$$q_e = \frac{x}{m} = k_f c_e^{\frac{1}{n}} \quad (2)$$

The isotherm coefficient in relation to the amount of adsorbed according to $L/g = kf$; The adsorption intensity is that changes with the non-uniformity of the material = $1/n$

One of the important studies in the adsorption process is the study of the effect of contact time on adsorption amount, which is known as kinetics studies. In order to study the mechanisms for controlling the adsorption process, the first-order kinetics

models (Lagergren) and second-order kinetics models (Ho et al) will be investigated. The Lagergren kinetics model is represented by Equation 3 [10].

$$\text{Log}(q_e - qt) = \text{log} q_e - (k_1 t / 2.303) \quad (3)$$

The equilibrium adsorption capacity as $\text{mg/g} = q_e$; The amount of cadmium adsorbed at time t according to $\text{mg/g} = qt$; The adsorption constant is according to $\text{min}^{-1} = k_1$

The Ho et al. kinetics model is represented by Equation 4 [10].

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2 + \frac{t}{q_e}} \quad (4)$$

The equilibrium adsorption capacity as $\text{mg/g} = q_e$; The amount of cadmium adsorbed at time t according to $\text{mg/g} = qt$; The adsorption constant is according to $\text{g. mg}^{-1} \text{min}^{-1} = k_2$

The efficiency of all models was evaluated using Root Mean Square Error (RMSE) and Coefficient of Determination (R^2) statistic parameters. The statistical indices RMSE and R^2 are defined as equations 5 and 6.

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^n (s_i - o_i)^2}{n}} \quad (5)$$

$$R^2 = \left(\frac{\sum_{i=1}^n (o_i - \bar{o})(s_i - \bar{s})}{\sqrt{\sum_{i=1}^n (o_i - \bar{o})^2 \times \sum_{i=1}^n (s_i - \bar{s})^2}} \right)^2 \quad (6)$$

The RMSE value indicates how much the predictions have estimated the measurements more or less. Whatever the value of the indicator is closer to zero, the better (the difference between the predicted and measured values is lower) [13]. The well-known R^2 statistic, or the (multiple) coefficient of determination, pertains to the proportion of variance in the response variable explained by a fitted model relative to simply taking the mean of the response. In other words, it describes how well the model fits the data. An R^2 close to 1 implies an almost perfect relationship between the model and the data, whereas an R^2 close to 0 implies that just fitting the mean is equivalent to the model fitted [13].

Results and Discussion

Use of eggshell as adsorbent in various studies

Asgari et al (2013) investigated the removal of cyanide by eggshell as low-cost adsorbent [16]. In this experimental study, the capability of ES to adsorb cyanide ions was conducted using a series of batch tests in a shaker-incubator instrument. For each batch run, 100 mL of solution containing a known initial concentration of cyanide and with the preferred level of pH was shaken. The effects of selected parameters such as pH (11-3), reaction time (60-5 min) cyanide concentrations (150-50 mg/L) and the adsorbent dosage (2-0.25 g/L) were investigated on the removal cyanide as a target contaminate. Chemical

composition ES were analyzed using a Philips model XL- 30 scanning electron microscope (SEM) with energy-dispersive X-ray microanalysis (EDX). The specific surface and pore size distributions of ES were measured via Brunauer-Emmett-Teller (BET) isotherm and Barrett-Joyner-Halenda (BJH) methods using a Micrometrics particle size analyzer. The concentration of cyanide in solution before and after treatment was determined using the titrimetric method as described in the standard methods. Analysis of the ES component using the EDX technique showed that the main part of it consisted of calcium and its other components were magnesium, iron, aluminum and silicate. The experimental data showed that the maximum cyanide removal occurred at pH of 11, adsorbent dose (0.5 g/L) and 40 min contact time. The kinetic evaluation indicated that the pseudo-second-order kinetic had the best fit to the experimental results predicting a chemisorptions process. The equilibrium adsorption of cyanide onto ES was well represented by the Langmuir equation. As a result, ES as waste materials was revealed as a very efficient and low-cost adsorbent and a promising option for removing cyanide from industrial wastewaters. Bafkar and Babeli (2019) investigated the nitrate removal from aqueous solutions by eggshell nanostructure adsorbent [17]. In this study, the effects of factors such as pH, adsorbent mass, contact time and initial concentration of nitrate were studied. Isotherm models (Langmuir and Freundlich) and kinetic models (Lagergren and Ho and colleagues) were used to examine the adsorption process. The results showed that for the adsorbent, the balance time after 30 minutes and maximum nitrate adsorption at pH=5 were obtained. By increasing the adsorbent mass from 0.3 to 0.5 gram, the removal efficiency increased from 96.01 to 97.24 percent, but with an increase in adsorbent content from 0.5 to 1.6 gram, there was a significant difference in the adsorption efficiency Failed. By increasing the concentration of dissolved nitrate (5.120 mg/l), the removal efficiency decreased from 99.42 to 87.38%. Based on the results, the adsorption process was followed by the model of Ho (Pseudo second order kinetics), and the adsorption data was more consistent with Freundlich isotherm. The results of this study showed that egg shell nanostructure adsorbent has high potential for removal of nitrate ions from aqueous solutions. Daraei et al (2014) investigated the efficiency of eggshell membrane in removal of phenol from aqueous solution [18]. In this research the effect of various parameters such as pH, contact time, temperature, dosage of shell membrane, and initial concentration of phenol were investigated. Central composite design (CCD) was applied to evaluate the effect of these variables. The chemical and physical characteristics of eggshell membranes were studied through SEM and XRF analysis. The results indicated that the optimum values for pH, dosage of shell membrane, contact time, temperature, and initial concentration for phenol sorption were 3.63, 3.78 g, 115.50 min, 20 °C and 5 mg/L, respectively. The results of the CCD analysis showed that pH and phenol concentrations are fundamental parameters affecting the efficiency. Results showed that eggshell, as a solid waste of the food industries, can be used

as an effective sorbent for removal of phenol and other organic pollutants from aqueous solutions. Ghaneian et al (2009) investigated the application of eggshell as a natural sorbent for the removal of reactive red 123 dye from synthetic textile wastewater [19]. This study is an applied- experimental research which was performed in laboratory scale and in environmental chemistry laboratory of Baqiyatallah (a.s) university of medical sciences. Eggshell as a sorbent was prepared in laboratory condition (20-25°C) and pulverized by standard ASTM sieves. The effective size (D_{10}) and D_{60} were 3 and 5.1mm, respectively and uniformity coefficient (UC) was 1.7. The concentrations of dye in wastewater were 25 and 50 mg/l. In this study increasing of adsorbent dose from 1 to 5 g/100ml led to increase of the adsorption efficiency from 48 to 80.7 %. The maximum adsorption took place in first 60min of reaction. With increasing the temperature up to 45°C the pollutant adsorption was increased and increasing of pH from 5 to 8 led to increase of process efficiency from 30 to 48%. Also absorption characteristics of this pollutant on eggshell accommodated with Langmuir isotherm. Eggshell can be used as a natural adsorbent in water and wastewater treatment. This adsorbent is an appropriate media for the treatment of textile wastewater that usually have alkaline condition and high temperature.

The results obtained from laboratory research

Figure 1 indicated the effect of pH on cadmium adsorption function. The changes range of pH is 2 to 10. Figure 1 shows that the highest adsorption efficiency of cadmium is 94% and occurs at pH =8. By increasing pH from 2 to 8 the adsorption efficiency of cadmium increases. At low pH the proton is high and the ion exchange sites in the adsorbent are filled by the proton and the proton competition prevents the adsorption of cadmium by the adsorbent. However, with increasing pH due to less proton competition with cadmium, the amount of cadmium adsorption by the adsorbent increases. But by increasing pH (more than 8) the adsorption efficiency decreases, so that at pH =10 adsorption efficiency is 60%. At pH greater than 8, the concentration of hydroxide anions increases, which reduces the cadmium adsorption by the adsorbent.

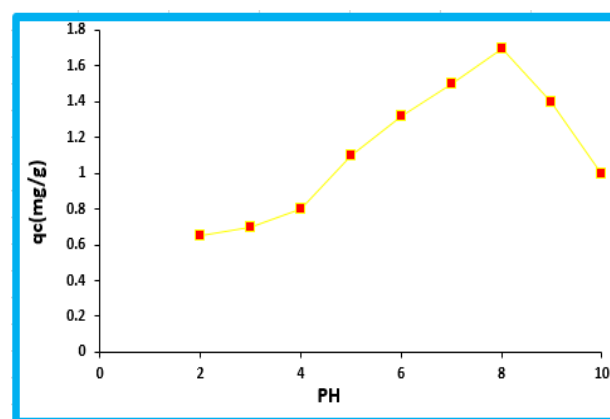


Figure 1- Changes in pH compared to cadmium adsorption efficiency by eggshell

Figure 2 indicated the effect of adsorbent amount (eggshell powder) on the cadmium adsorption efficiency with a concentration of 30 mg/L. Tests were executed in solutions of 100 ml volume. The results indicated that by increasing the amount of adsorbent (eggshell powder) from 1 g to 40g, the adsorbent contact increases with cadmium ions and enhanced the cadmium surface adsorption. The cadmium adsorption efficiency was decreased, when the amount of adsorbent exceeds 40g. Because, by increasing the amount of adsorbent (eggshell powder) in the solution, the specific surface of the adsorbent particles decreases. By decreasing the specific surface of the adsorbent particles decreases the cadmium adsorption efficiency.

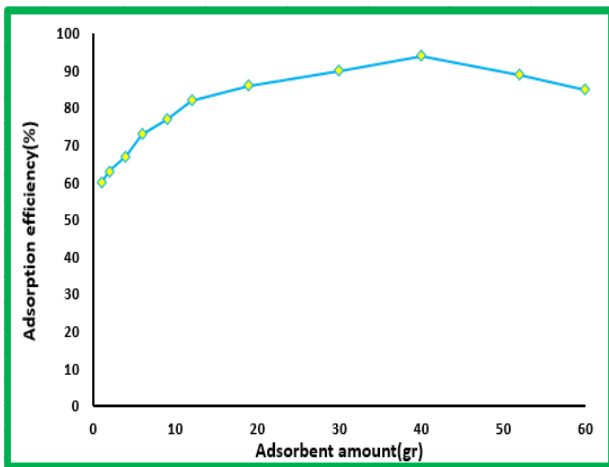


Figure 2- Changes in adsorbent amount compared to cadmium adsorption efficiency by eggshell

Figure 3 shows the fitness of kinetics models of cadmium adsorption by eggshell in optimum pH. Too, the fitness results of the models are reported in Table 1. The analogy of the results indicated that Ho et al. model with premier determination coefficient ($R^2=0.96$) and minor root mean square error (RMSE=0.06) compared to the Lagergren model ($R^2=0.89$, RMSE=0.15) demonstrates test data superior. Too, the results indicated that the Lagergren model was more prosperous in computing the amount of q_e (1.63 mg/g) compared to Ho et al. model (1.75 mg/g). pursuant to Fig. 3, the quantity of adsorption increases with augmenting retention time. In addition, with enhancing the contact of cadmium ions with eggshell, the content of adsorption increases. At 120 min after contact of eggshell powder and cadmium solution, the adsorption process attained balance. enhancing the retention time after this time does not affect the value of adsorption.

Table 1-Parameters of kinetics models of cadmium adsorption by eggshell

q _{experimental}	Lagergren model				Ho et al. model			
	RMSE	R ²	K ₁	q _e	RMSE	R ²	K ₂	q _e
1.70	0.15	0.89	0.04	1.81	0.06	0.96	0.05	1.96

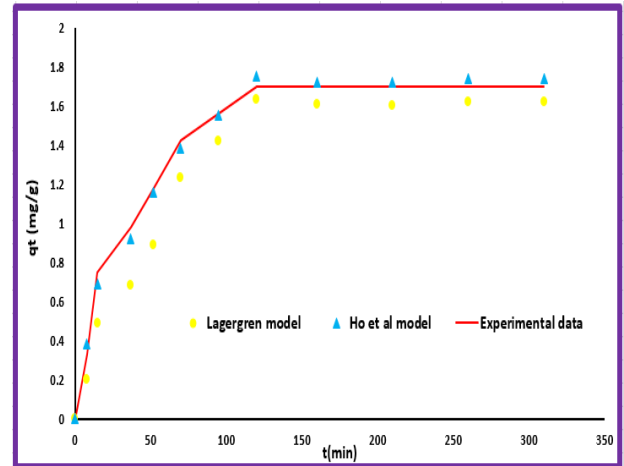


Figure 3-The fitting of kinetics models on experimental data of cadmium adsorption by eggshell

Figure 4 shows the fitness of isotherm models of cadmium adsorption by eggshell. Too, the fitness results of the models are reported in Table 2. Comparing the Langmuir and Freundlich isotherm for cadmium adsorption by eggshell indicated that Freundlich isotherm ($R^2=0.97$, RMSE=0.08) was rather appropriate than Langmuir isotherm ($R^2= 0.87$, RMSE=0.52) in explaining adsorption process. The parameter b in the Langmuir model represented the most eggshell capacity for cadmium adsorption at its surface. In this research, parameter b was 13.59 mg/g.

Table 2-Parameters of isotherm models of cadmium adsorption by eggshell

Freundlich isotherm				Langmuir isotherm			
RMSE	R ²	K _f	n	RMSE	R ²	K _L	b
0.08	0.97	0.76	0.52	0.52	0.87	0.15	13.59

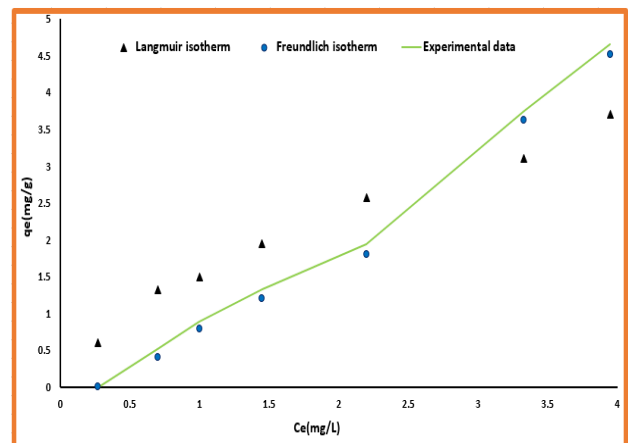


Figure 4- The fitting of isotherm models on experimental data of cadmium adsorption by eggshell

Conclusion

Cadmium is a natural element in the Earth's crust and is commonly found as a mineral in combination with other

elements such as oxygen (cadmium oxide), chlorine (cadmium chloride), or sulfur (sulfate cadmium). It is transmitted to humans by the food chain. Cadmium first goes to the liver by blood. In the liver, cadmium binds to proteins and forms a complex that goes to the kidneys and causes various diseases. Much research has been done to find low-cost adsorbents to remove cadmium from water. The eggshell as the most abundant adsorbent in the world for cadmium removal has been investigated in this study. Pursuant to the results of this research, optimum pH for cadmium adsorption by eggshell is 8. The results of adsorption kinetics test indicated that as the retention time enhancement, the adsorption efficiency increases, and the equilibrium time for this research is 120 minutes. At the optimal equilibrium time and pH, the most adsorption amount was obtained 1.70 mg/g. In addition, the results indicated that Ho et al. model describes adsorption kinetics data superior than Lagergren model. The results of isotherm studies indicated that the Freundlich model has a superior fit for adsorption experimental data.

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